

1 Introduction

1.1 A brief history and motivation

Atmospheric chemistry has had a remarkably successful history given the scale and complexity of the subject. The foundation of that success lies in the synergy between the three branches of the field: Observational measurements, laboratory experiments, and atmospheric models. Each branch depends on and supports the other leading to a robust interwoven system for verification or dismissal of new hypotheses. The laboratory branch of atmospheric chemistry started to make significant progress in the 17th–19th centuries with the pneumatic chemists such as Antoine Lavoisier, Joseph Priestly, Daniel Rutherford, and Henry Cavendish. Cavendish was the first to recognize that air was made up of 1 part phlogisticated and 4 parts dephlogisticated air, i.e., ~20% oxygen (O₂) and ~80% nitrogen (N₂).¹ He was also able to identify another component that made up no more than 1/120 of the total volume. That component would later be identified as argon (Ar), an unknown element at the time. These major components of the atmosphere were all known early on, but it would be a while until the impact of trace species well beyond their small concentrations could be appreciated.

One of the next discoveries came in the late 19th and early 20th century with the discovery of the ozone (O₃) layer. Ozone absorption in the atmosphere was first proposed by William Hartley after his laboratory experiments on O₃ provided a candidate that matched the absorption in the atmosphere observed by Cornu.^{2,3} Careful measurements and observations by Charles Fabry and Henri Buisson confirmed the assignment as well as estimated a thickness of the layer.⁴ Lastly, Sydney Chapman developed the first model

of how and where the O₃ formed in the atmosphere; the Chapman mechanism shown below is the first example of an atmospheric cycle.⁵



Ozone would be more infamously discovered as one of the main photochemical components of atmospheric smog through the research of Arie Haagen-Smit in the 1940 – 50s.^{6,7} This work combined observational studies of pollution effects on crops and rubber in the Los Angeles area, with laboratory studies to recreate the main component of the pollution.⁸ Haagen-Smit's work was the first to recognize that the combination of trace hydrocarbons, nitrogen oxides, and light led to photochemical O₃ pollution.

The importance of stratospheric O₃ came to dominate the public's understanding of O₃ from the 1980s onward due to the observation and explanation of the polar stratospheric "ozone hole," through the combined efforts of all the branches of atmospheric science. The unraveling of the chemistry and dynamics involved in polar stratospheric O₃ loss combined with the political implementation of scientific recommendations remains one of the best examples of rigorous scientific work positively influencing public policy.^{9,10}

At the same time work continued on understanding the mechanism for O₃ production in the troposphere. One irony of the field is that similar cycles determined to consume O₃ up in the stratosphere where it is beneficial to life, were determined to produce O₃ in the troposphere where it is hazardous to life. The central cycle to the production of O₃ in the troposphere is the coupling of NO_x (NO and NO₂) and odd

oxygen (O_3 and $O(^3P)$) through reactions (1.4) – (1.6) and the Chapman mechanism.^{11,12}

Photolysis of NO_2 provides oxygen atom in its ground electronic state, $O(^3P)$.



$O(^3P)$ then forms O_3 through reaction (1.2) or a null cycle occurs if NO reacts with O_3 to reform NO_2 .



Together these reactions during the daytime lead to a photostationary state O_3 concentration given by equation (1.6),

$$[O_3] = \frac{j_{NO_2}[NO_2]}{k_{1.5}[NO]} \quad (1.6)$$

where j_{NO_2} is the first-order rate coefficient for photodissociation of NO_2 . The implication of equation (1.6) is that any production of NO_2 which does not come from reaction (1.5) will lead to a net production of O_3 . Hydrocarbons (RH) and their resulting peroxy radicals (RO_2) form a critical link in smog formation by acting as oxidants to recycle NO back to NO_2 through reaction (1.7) without the consumption of O_3 .



Alkoxy radicals (RO) formed in this reaction continue the cycle through further reactions.



Reformation of the hydroxyl radical (OH) in reaction (1.9) is important because OH is the initial oxidant that reacts with RH to create the RO_2 .

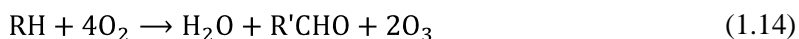




OH is initially formed in the troposphere by reaction of excited atomic oxygen O (¹D), from photolysis of O₃, with water vapor (H₂O).



The flux of light reaching the troposphere at wavelengths less than 300 nm is small so the recycling of OH through the NO_x chemistry is critical to insuring that there are sufficient radicals to oxidize the RH emitted to the atmosphere.¹³ In total, RH in the presence of NO_x and sunlight leads to the buildup of O₃ through the net reaction:^{14,15}



The net scheme just described is one important end of many possible variants that have been systematically worked out through the complimentary efforts of all three branches of atmospheric chemistry. Much like the stratospheric work, but without the global treaty, this work collectively has led to government policy aimed at reducing pollution. Given the critical nature of RH for O₃ production initial pollution control efforts were directed at reducing RH emissions. However further work showed that an underestimation of the contribution of the biosphere to total RH had misled people into thinking that O₃ was limited by RH emissions. In fact when better measurements of the large biosphere contribution are used in the models it turns out that many areas of the country are limited by NO_x, despite the large concentrations emitted from automobiles, and stricter NO_x emission controls will be most effective in reducing O₃.¹⁶⁻¹⁸

These discoveries highlighted the need for better understanding of the RO₂ chemistry in the absence of NO_x; both in order to model the background troposphere

where there is less anthropogenic influence, and also to understand the types and spatial extent of reactions that become important under NO_x-limited regimes.

1.2 Thesis work

The main focus of this work is laboratory studies of RO₂ reactions when no NO_x is present. Reaction with HO₂ (daytime mixing ratios of ~ 1–10 pptv)¹⁹ is the dominant fate of RO₂ in the atmosphere at low NO_x.



The hydroperoxide products (ROOH) are reservoir species of reactive radicals. Removal of ROOH can occur by wet and dry deposition or participation in aerosol chemistry.

Alternatively they can undergo photolysis or reaction with OH to recycle the radicals for further atmospheric reactions. Peroxy radical self reactions can also be important, especially the HO₂ self reaction forming another radical reservoir species.



The RO₂ self reactions have much smaller rate coefficients so their individual reactions play less of a role in the atmosphere, but the sum total of all their reactions cannot be ignored. In laboratory experiments RO₂ self reactions are important to account for when studying the atmospherically important RO₂ + HO₂ reactions because of interfering secondary chemistry.

In Chapter 2 the HO₂ and C₂H₅O₂ system of reactions, (1.15) – (1.17), were investigated. Radical reactions are difficult to isolate leading to the almost inevitable difficulty of multiple reactions occurring at once. Self reactions of RO₂ further

complicate matters by producing secondary HO₂ through one of their product channels. Time resolved spectroscopy specifically targeting each reactant was used to measure the rate coefficients for the self and cross reactions of HO₂ and C₂H₅O₂, as well as the product branching fraction of the C₂H₅O₂ self reaction responsible for the secondary HO₂. Chapter 3 looks further at self reactions of CH₃O₂, C₂H₅O₂, and C₃H₇O₂, but using a different experimental technique. Photoionization mass spectrometry was used to measure branching ratios for different product channels of these self reactions by monitoring all of the stable reactions products in time.

Nucleation observed in low temperature experiments on the HO₂ self reaction is the subject of Chapter 4. Radical chemistry is the main driver of gas phase atmospheric cycles, but is not currently thought to be at the center of new particle formation. Recently discovered radical-molecule complexes between HO₂ and a number of species, including methanol, water, and acetone, might be good candidates for particle seeds at low temperature due to the stability of their hydrogen bonds. Most of the nucleation work described is on the HO₂ – methanol complex, but all three were investigated. Lastly, Chapter 5 goes through the experimental calibrations and general procedures that went on throughout all this work.

1.3 Challenges ahead

While much is known about peroxy radical chemistry, some critical gaps in our knowledge remain. A recent field study in China was unable to model the observed distribution of HO_x between OH and HO₂, leading to the need for new laboratory experiments to shed light on reactions that could shift the predicted distribution.²⁰ Recent lab work has shown that other product channels of reaction (1.15), producing both OH

and O_3 , are important when the RO_2 contains a carbonyl functional group.^{21,22} These reaction channels directly recycle the radicals without going through a reservoir species leading to a very different net reaction. Peroxy radical chemistry is also proving important in understanding secondary organic aerosol (SOA), a major influence on climate and health. Formation of SOA from isoprene, the largest non-methane hydrocarbon emitted to the atmosphere, is greater at low or no NO_x in laboratory experiments,²³ and epoxides formed in the OH oxidation of ROOH were determined to be the main source of the SOA growth.²⁴ The work showing this used detailed laboratory experiments to wrap up a mystery discovered by observational work done in areas with high isoprene emissions and unexplained HO_x chemistry. The growing importance of peroxy radical chemistry to SOA, the continued discovery of previously unknown gas phase reactions, and the discrepancies between models and observation show that there is still much to learn.

1.4 References

- (1) Cavendish, H. *Philosophical Transactions of the Royal Society of London* **1784**, 74, 119.
- (2) Cornu, A. *Compt. Rend.* **1879**, 88, 1101.
- (3) Hartley, W. N. *Chemical News* **1880**, 42, 268.
- (4) Fabry, C.; Buisson, H. *Comptes Rendus Hebdomadaires Des Seances De L Academie Des Sciences* **1913**, 156, 782.
- (5) Chapman, S. *Quarterly Journal of the Royal Meteorological Society* **1932**, 58, 11.
- (6) Haagensmit, A. J. *Industrial and Engineering Chemistry* **1952**, 44, 1342.
- (7) Haagensmit, A. J.; Darley, E. F.; Zaitlin, M.; Hull, H.; Noble, W. *Plant Physiology* **1952**, 27, 18.
- (8) Pitts, J. N., Stephens, E.R. *Journal of the Air Pollution Control Association* **1978**, 28, 516.
- (9) The 1987 Montreal Protocol on Substances that Deplete the Ozone Layer; United Nations Environment Programme, O. S., Ed., 1987.
- (10) Parson, E. *Protecting the ozone layer : science and strategy*; Oxford University Press: New York, 2003.
- (11) Chameides, W. L.; Walker, J. C. G. *Journal of Geophysical Research* **1973**, 78, 8751.
- (12) Crutzen, P. *Pure and Applied Geophysics* **1973**, 106, 1385.
- (13) Jacob, D. J. *Introduction to Atmospheric Chemistry*; Princeton University Press: Princeton, 1999.
- (14) Fishman, J.; Solomon, S.; Crutzen, P. J. *Tellus* **1979**, 31, 432.
- (15) Liu, S. C.; Trainer, M.; Fehsenfeld, F. C.; Parrish, D. D.; Williams, E. J.; Fahey, D. W.; Hubler, G.; Murphy, P. C. *Journal of Geophysical Research-Atmospheres* **1987**, 92, 4191.
- (16) Chameides, W. L.; Fehsenfeld, F.; Rodgers, M. O.; Cardelino, C.; Martinez, J.; Parrish, D.; Lonneman, W.; Lawson, D. R.; Rasmussen, R. A.; Zimmerman, P.; Greenberg, J.; Middleton, P.; Wang, T. *Journal of Geophysical Research-Atmospheres* **1992**, 97, 6037.
- (17) Sillman, S.; Logan, J. A.; Wofsy, S. C. *Journal of Geophysical Research-Atmospheres* **1990**, 95, 1837.
- (18) Trainer, M.; Williams, E. J.; Parrish, D. D.; Buhr, M. P.; Allwine, E. J.; Westberg, H. H.; Fehsenfeld, F. C.; Liu, S. C. *Nature* **1987**, 329, 705.
- (19) Seinfeld, J. H., Pandis, S.N. *Atmospheric Chemistry and Physics*; John Wiley and Sons: New York, 1998; pp 82.
- (20) Hofzumahaus, A.; Rohrer, F.; Lu, K. D.; Bohn, B.; Brauers, T.; Chang, C. C.; Fuchs, H.; Holland, F.; Kita, K.; Kondo, Y.; Li, X.; Lou, S. R.; Shao, M.; Zeng, L. M.; Wahner, A.; Zhang, Y. H. *Science* **2009**, 324, 1702.
- (21) Dillon, T. J.; Crowley, J. N. *Atmospheric Chemistry and Physics* **2008**, 8, 4877.
- (22) Hasson, A. S.; Tyndall, G. S.; Orlando, J. J. *Journal of Physical Chemistry A* **2004**, 108, 5979.

(23) Kroll, J. H.; Ng, N. L.; Murphy, S. M.; Flagan, R. C.; Seinfeld, J. H. *Environmental Science & Technology* **2006**, *40*, 1869.

(24) Paulot, F.; Crouse, J. D.; Kjaergaard, H. G.; Kurten, A.; St Clair, J. M.; Seinfeld, J. H.; Wennberg, P. O. *Science* **2009**, *325*, 730.